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Показано, що застосування спеціальної обробки біосумісних порошків перед плазмовим запиленням, що полягає в закріпленні дрібних частинок на великих гранулах, сприяє підвищенню рівномірності пористої структури, міцності, відкритої пористості покриття і більш розвиненій морфології його поверхні, а також збільшенню площі контакту дотичних поверхонь (ендопротез і кісткова тканина) при його додатковому наноструктуруванні

Ключові слова: біосумісні матеріали, пористість, кристалічна структура, плазмове запилення, гідроксиапатит, оксид алюмінію, термомеханічна обробка

Показано, что применение специальной обработки биосовместимых порошков перед плазменным напылением, заключающейся в закреплении мелких частиц на крупных гранулах, способствует повышению равномерности пористой структуры, прочности, открытой пористости покрытия и более развитой морфологии его поверхности, а также увеличению площади контакта соприкасаемых поверхностей (эндопротез и костная ткань) при его дополнительном наноструктурировании

Ключевые слова: биосовместимые материалы, пористость, кристаллическая структура, плазменное напыление, гидроксиапатит, оксид алюминия, термомеханическая обработка

УДК 621.762; 616-089.843; 616.31

IMPROVING THE QUALITY OF BIOCOMPATIBLE PLASMA-SPRAYED INTRAOSSEOUS IMPLANT COATING

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1. Introduction

Modern oral medicine and traumatic surgery widely uses biocompatible materials based on aluminium oxide and calcium phosphate ceramic for elimination of osteal defects of different etiology. The major drawback of such is low mechanical resistance [1-4]. A solution to this problem is plasma spraying of powder aluminium oxide and calcium phosphate materials in order to obtain ceramic coating of implants. Resulting coating shall be of certain mechanical, physical and chemical, and biological characteristics to provide desired interreacting with internal milieu [5,6].

It is known that pore size in porous frame is defined by the size of particles composing it [7,8]. We have developed and are using a technology of plasma spraying for ceramic coating of titanium endosteal implants with porous titanium intermediate layer of titanium powder consisting of 250 μm particles. This technology supposes usage of biocompatible powder consisting of 40 to 120 μm particles [9] as the coating is necessary to be heavy porous for bone tissue and blood vessel budding into the implant. However the space of 40-120 μm is wide enough for a coating with smooth porous structure. Hydroxyapatite powder (HA) possesses binding properties, that is why its sieving presents certain difficulties, and powder size gap decreasing is not reasonable due to essential material losses.

The purpose of the work is improvement of functional characteristics of biocompatible plasma-sprayed implant coating by means of smoothing their porous structure and stabilizing their crystalline texture.

2. Experimental procedure and analysis of experimental findings

There is a technique of powder quality improvement based on its grain size distribution resulting in elimination of ultrafine and fine fraction consisting in thermomechanical processing (TMP) by means of prolonged annealing followed by a slight grinding [10,11]. During TMP fine and the most active particles of the original powder adhere together and to the larger particles and in the process of the following slight grinding do not detach as independent particles.

Large conglomerates (60-70 μm) which are not active during TMP dissolve to finer particles of the base size in the process of grinding. Thus, previously annealed and grinded powder becomes less polydispersed than the basic one and results in a more solid structure of a porous frame.

In the process of spraying ~ 40 μm fine particles they are warmed up greatly, though possessing low kinetic energy they lose shape very little when bumping against the support and do not adhere to it firmly as a result. When increasing particle size above 40 μm their mass and inertial energy grow up, that is why the particles slow down less and bump against the support with a higher speed. This leads to a measurable deformation, contacting area extending, increase of tension and adhesion between the coating and the support as the final result.

Based on the above the proposed TMP of endosteal implant biocompatible powder consisting in creation of base powder combined particles for spraying by means of fastening (immobilization) of ~ 40 μm fine particles to larger ones leads also to increase of adhesion to titanium-based coating with an intermediate layer of titanium powder.

In the process of plasma spraying in high temperature stream heat-conducting path from a fine particle to a large one preserves a number of fine particles from a complete meltdown. Also when bumping against the support a combined particle splits by separation a fine particle from a large one. Herewith it is assumable that a fine particle possessing kinetic energy and tension of a large particle breaks into nanosized particles. Inclusion of biocompatible coating of finer nanoscaled ceramic particles into the structure is reasonable considering its functional characteristics improvement due to increase of active contacting area between the implant and the bone.

To stabilize parameters of aluminium oxide powder the following methodics was tested: levelling of differently-sized particles dispersion within implant bulk by means of prolonged thermal processing of aluminium oxide powders (Al_2O_3) and their blenders followed by grinding [12].

A quality assessment methodics of Al_2O_3 powder processing was developed. The quality factor is compressive strength of trial tablets sintered from it.

Trial tablets of 8 mm in diameter are pressed from Al_2O_3 powders or their blenders with a plasticity agent supplement in amounts of 2% of tablet mass in a press mould applying 0,32 hPa strain and are sintered in continuous operation hydrogen pusher furnaces with temperature control and optical pyroscope LOP-72 by 1750°C during 10 min and then tested for compressive strength in a breaking machine. A БВ-22 enamel was used as a plasticity agent.

In the process of experiment heavy-grain aluminium oxide powders composed of spheroid ~ 40-60 μm particles and electrovacuum Al_2O_3 composed of ~ 1-3 μm particles in the amounts of 80% of coarse powder and 20% of fine powder were intermixed in ceramic evaporation bowl during 15-20 min.

Freely poured Al_2O_3 powder blenders were annealed in a temperature range between 1100 and 1500^0C in hydrogen during 3h and then crumbled in a ceramic mortar box during 20 min.

The results of compressive strength tests presented in table 1 prove that sample solidity increased after TMP. Maximum strength of samples is achieved by annealing of Al_2O_3 powders by temperature 1200-1250^0C which indicates proportional and the most effective particle setup (table 1).

Previously annealed and crumbled Al_2O_3 powder blenders become more homogeneous in grain distribution which is caused by dissolution of fine powder ultradisperse fraction (~1 μm or less) which is fastened to microgranules after powder blender processing (fig. 1).

Table 1

Test results of Al_2O_3 powder blender samples annealed by different temperatures

Blender anneal temperature, T^0C	Sample compressive strength, σ yield point, kg/mm^2
No anneal	17,4
1100	22,2
1200	35,5
1250	35,4
1300	28,5
1400	25,6
1500	24,8

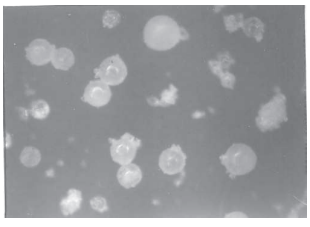

Fig. 1. Alundum powder blenders of different grain distribution after TMP, × 300

To additionally assess mechanical resistance and service life of Al_2O_3 powder blenders a thermal cycling strength test was done. For that reason a suspension was prepared in a binder and poured into a spare cavity in reheating assembly frame after placing a heater therein. Sample sintering was executed in hydrogen medium by 1750°C during 10 min. Tests were done in glass vacuum diodes (with vacuum not lower than $3 \cdot 10^{-7}$ Mmhg) in cycling mode (nominal stress = 9V - 3 min on, 7 min off) by temperature 1470°C (table 2).

Comparison of table 1 and table 2 results shows that usage of homogeneous structure of Al_2O_3 powder blenders which is achieved with the help of TMP by 1250°C facilitates obtaining of maximum service life coating consisting of these blenders, and their high strength during cycling tests.

Thus, TMP of aluminium oxide powders by 1200-1250°C leads to levelling of grain distribution which improves functional characteristics of plasma sprayed biocompatible material as a result of smoothing their porous and scaffold structure.

The developed technology of Al_2O_3 powder TMP may also be used during preparation of calcium phosphate ceramic biocompatible powders before plasma spraying.

Table 2

Thermal cycling test results of intermediate layers consisting of Al_2O_3 powder blenders of different grain distribution annealed by different temperatures

Anneal temperature of Al_2O_3 powder blenders, T,°C	Number of cycles (N, items) needed for obtaining		
	filler shrinkage	insulation substance destruction	
		filler cracking	peeling off the frame
No anneal	450	1500	-
1200	800	no	4100
1250	790	no	4200
1300	150	no	3500
1500	100	Burnt out after 250 cycles	Burnt out after 250 cycles

TMP of hydroxyapatite polydispersed powders before plasma spraying executed for the purpose of grain distribution and, subsequently, porous structure levelling was conducted in temperature range between 800 and 1000°C. The powders were annealed in muffle furnace during 3h and then crumbled in a ceramic mortar box during 20 min. Temperature control was maintained with the help of thermocouple.

The resulting powders were sprayed onto Ti Grade 1 titanium samples with an intermediate layer of titanium powder composed of 250 μm particles.

Metallographical and fractographical analysis of the coating conducted with the usage of biological light microscope (model 10) and upgraded research metallographic microscope (model 8M) and profilograph-profilometer (model 170623) showed that TMP appliance by 800, 900 and 1000°C results in a smoother structure with larger pores (fig. 2), with their size increasing by anneal temperature rise adequately to surface morphology mutation (table 3).

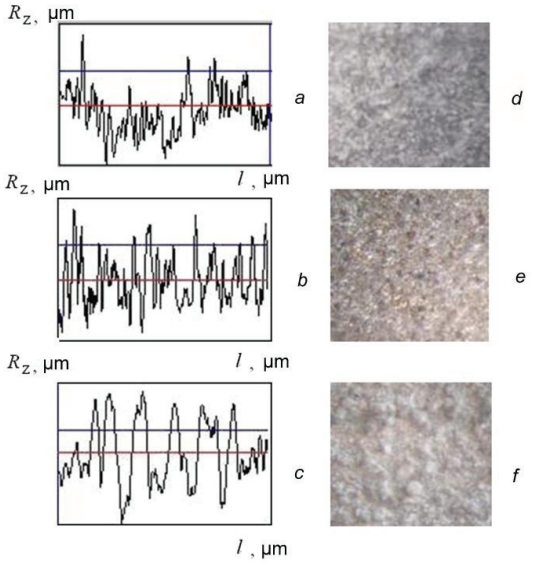

Fig. 2. Pattern (*a,b,c*) and external surface view (*d,e,f*) of hydroxyapatite (HA) coating on titanium with an intermediate layer composed of titanium powder in the process of HA spraying in the basic state (*a,d*) and after annealing by 800 °C (*b,e*) and 1000 °C (*c,f*) surface view scale — 90 ×, pattern scale — 150 ×

Table 3

Impact of hydroxyapaxite powder anneal temperature on asperity (R_z) and size of open pore channels of a plasma sprayed surface

Sintering temperature TMP, T, °C	Parameter $^*R_z$, μm	Open pore channel size, **d, μm
No processing	45,8	5-7
800	49,9	7,8-19,6
1000	104	20-39,2

$^*R_z$ – inequality hight measured by 10 points

** – pores where the intermediate layer in bright field was seen during metallographical analysis were treated as open pore channels.

With an anneal temperature rise during TMP particle coarsening typical for TMP results in a more developed coating surface morphology and increase of open pore channel size (table 3).

Anneal temperature impact tests were also conducted during HA powder TMP concerning the powder structure, crystallinity, phase composition, and binding properties through X-ray diffraction and electron-microscopic analysis (fig. 3, 5). X-ray diffraction and phase powder analyses were executed with the usage of general purpose X-ray diffractometer (model 3). Sprayed surface *morphology* and laminate pattern were examined with a MIRA II LMU scanning

electron microscope (SEM) released by TESCAN company (Czech Republic) with a ЭДС Ynka Energy 350 attachment by accelerating voltage of 20-30 kV. For this purpose a thin aurum conductor layer (10-20 nm) was spread onto the samples applying magnetron sputtering method.

TMP of HA base powders in a temperature range between 800 and 900^{0}C does not lead to powder phase composition mutation but leads to crystallinity degree change and inner stress decrease (table 4, fig. 4). HA in basic state is considerably amorphous and possesses an unstable structure. In the process of anneal in a temperature range between 800 and 1000°C HA crystallizes and its stresses are measurably lowered (fig. 4).

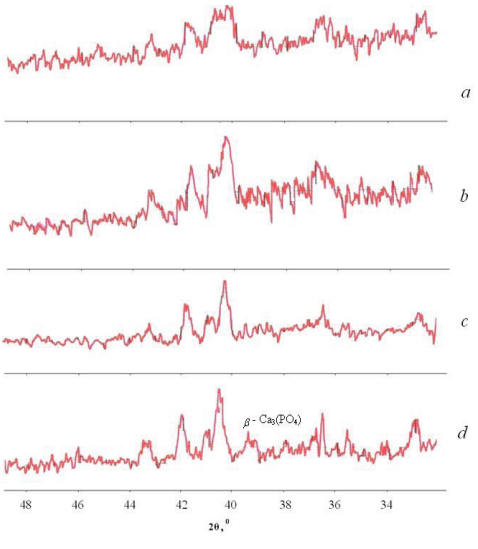

Fig. 3. HA powder diffraction patterns without TMP (*a*) and after TMP by: *b* — 800 ^{0}C; *c* — 900 ^{0}C; *d* —1000 ^{0}C

Table 4

TMP anneal temperature impact on HA characteristics

TMP temperature, °C	Binding properties (adhesion of powder to pestle)	Crystallinity degree*, %	Line occurence β - $Ca_3(PO_4)_2$ c *d* = 2,88 Å (2 θ = 39,5 ^{0})
No processing	yes	33	no
800	yes	39	no
900	yes	45	no
1000	no (flowing)	57	yes

** Crystallinity degree was defined by diffraction pattern reflex area and reflex and field total area ratio in angle interval 2θ between 39 and 44°*

Anneal by 1000°C results in a new phase formation – tricalcium phosphate – β – $Ca_3(PO_4)_2$ which is defined by an occurance of a new reflex on HA diffraction pattern (fig. 3 *d*, table 4).

Considerable particle enlargement of biocompatible material with an HA base by TMP temperature 1000°C leads to depreciation of sputtering quality caused by formation of large open pore channels (table 3) and, subsequently, notable uncovered areas of the intermediate layer.

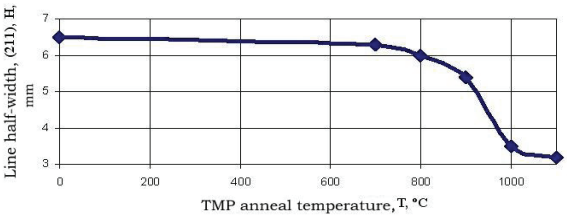

Fig. 4. Interdependence between line half-width (211) of HA powder diffraction pattern and TMP anneal temperature before plasma spraying

Thus a recommended HA powder TMP anneal interval lies between 800 and 900^{0}C.

Smoothing hydroxyapatite coating structure after TMP by 800^{0}C is proved also by electron microscopical structure tests (fig.5 *a,b*) [13]. At the fig. 5 traces on large particles can be seen where finer particles immobilized during TMP separated after bumping against the support. As a result, the structure of hydroxyapatite coating consists not only of 180 nm nanoparticles formed by splitting HA particles in the process of spraying, but also specific finer 40-60 nm nanoflakes (fig. 5 *d*). Splitting of HA particles that underwent TMP is presumably caused by their more crystallized structure.

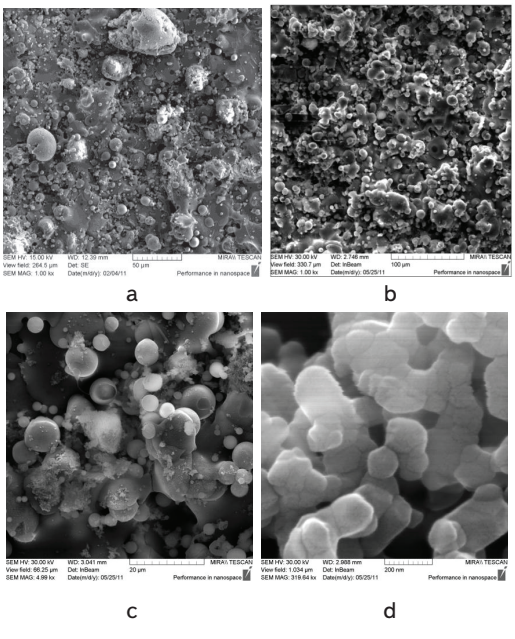

Fig. 5. SEM-images of plasma sprayed hydroxyapatite coating without TMP (*a*) and after TMP anneal by 800^{0}C (*b-d*)

3. Conclusions

Thus, the outcome of the tests are as follows:

1. Technologies of biocompatible aluminium oxide and hydroxyapatite powders were developed. The technologies lie in a prolonged anneal followed by grinding which provide elimination of polydispersed powder fine fraction, increase of an average particle size, and consequently an average pore size, and levelling the porous structure.

2. It was established that the developed method of structure smoothing provides increase of strength and service life of biocompatible aluminium oxide coating.
3. It was proved that hydroxyapatite powder TMP results in levelling the porous structure and forming a stable crystalline texture of plasma sprayed coating which facilitates its functional characteristics.

The reported study was funded by RFBR, research project No. 12-08-31217 mol_a.

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В статті описані дослідження структури та властивостей термозміцненого арматурного прокату марки Ст3ТГпс у потоці безперервних прокатних станів з використанням способу переривистого гартування. Проведений аналіз зміни мікротвердості по перетину арматурних стрижнів зі сталі Ст3Гпс по різним режимам термозміцнення

Ключові слова: структура, термозміцнений арматурний прокат, переривисте гартування, мікротвердість

В статье описано исследование структуры и свойств термоупрочненого арматурного проката из стали Ст3Гпс в потоке беспрерывных прокатных станов с использованием способа прерывистой закалки. Проведен анализ изменения микротвердости по сечению арматурных стержней из стали Ст3Гпс по различным режимам термоупрочнения

Ключевые слова: структура, термоупрочненый арматурный прокат, прерывистая закалка, микротвердость

УДК 669.268

СТРУКТУРА И СВОЙСТВА ТЕРМОУПРОЧНЕННОГО АРМАТУРНОГО ПРОКАТА ИЗ СТАЛИ СТ3ГПС

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